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# Studies on the Molecular Structures of BHC(1, 2, 3, 4, 5, 6-Hexachloro-cyclohexane) and their Related Compounds

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It was in 1825 that BHC was first synthesized<sup>(1)</sup>, and from 1943 to 1945 it was discovered that among the four isomers of BHC which were already known at that time, only  $\gamma$ -BHC has an exceptionally strong insecticidal activity.<sup>(2)</sup> Since then, BHC has been the focus of keen attention, and many studies have been made both from the pure academic field and from the standpoint of its application.

As to the structures of those isomers, various and thorough investigations have been made both from the standpoint of physical chemistry, such as X-ray analysis<sup>(4-10)</sup>, dipole moment investigation<sup>(11-21)</sup>, and electron diffraction investigation<sup>(22,23)</sup>, and from the field of organic chemistry.<sup>(24-29)</sup>

In parallel with these investigations, the authors<sup>(30,31)</sup> too have been investigating organic chemically the structures of the isomers of BHC and their related compounds such as 1,1,2,3,4,5,6-heptachlorocyclohexane (hepta), 1,1,2,3,4,4,5,6-, and 1,1,2,2,3,4,5,6-octachlorocyclohexane (Dichlorobenzene Hexachloride; octa). As a result they have discovered a new isomer of hepta with a melting point of 55~55.5° ( $\epsilon$ -form), and determined the structures of  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -BHC;  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -hepta; and  $\beta$ -p-, and o-octa. Although the results of the investigations have been reported in the magazine "The Bochu-Kagaku" ("The Scientific Insect Control") since 1949, this time, the authors wish to give a comprehensive report by way of completing the announcement of their studies.

## I. The Authors' Ideas of Determining the Molecular Configurations of BHC and their Related Compounds by Organic Chemical Method

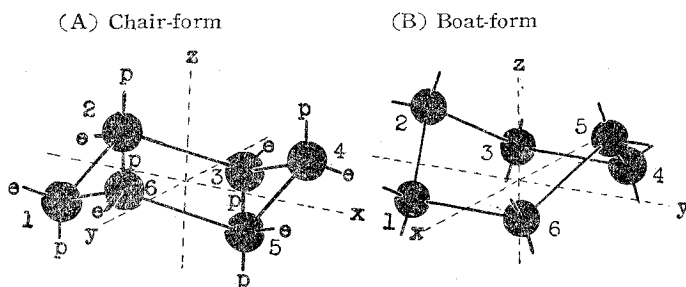


Fig.1 : Model of Cyclohexane Ring

As for the molecular structure of cyclohexane, when its carbon atoms are retaining their almost perfect tetrahedral valence angle, there are two possible

forms as shown in Fig.1; the so-called chair-form and boat-form, as has been pointed out by H.Sachse<sup>(32)</sup>. However, from the studies of electron diffraction measurement, Raman effect, infrared spectra, and the measurements of entropy, etc., it has been recently proved by O. Hassel et al.<sup>(33-35)</sup>, K. W. F. Kohlrausch et al.<sup>(36)</sup>, R. S. Rasmussen<sup>(37)</sup>, C. W. Beckett et al.<sup>(38)</sup>, K. Kozima et al.<sup>(39,41)</sup>, and T. Shimanouchi et al.<sup>(40)</sup> that the actual molecule of cyclohexane almost without exception, has a chair-form with the symmetry of  $D_{3d}$ . As a result, the difference among the isomers of BHC, hepta, and octa

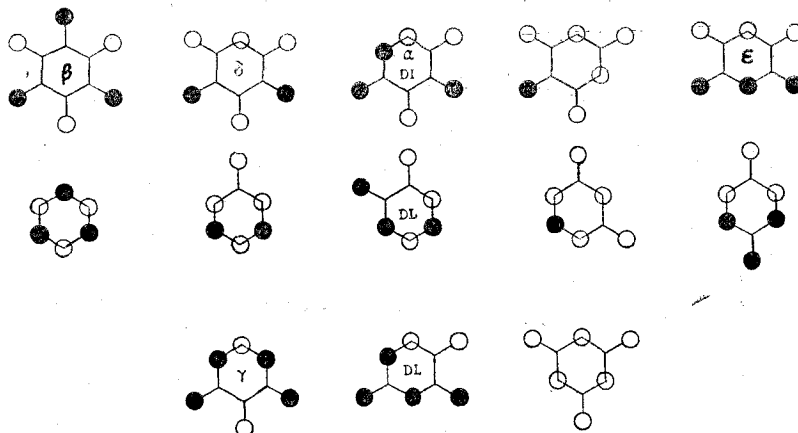


Fig. 2 : Geometrical Configuration of the Isomers of BHC.

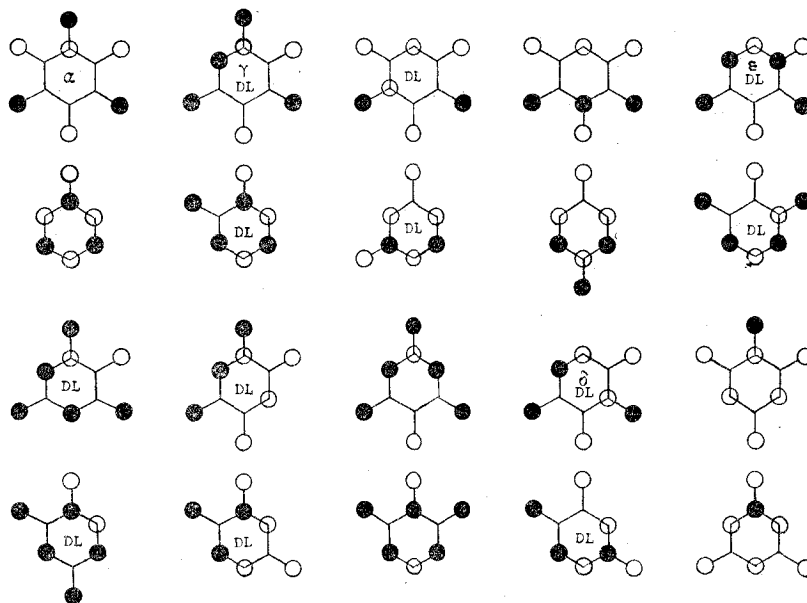


Fig. 3 : Geometrical Configuration of the Isomers of 1,1,2,3,4,5,6-Heptachlorocyclohexane (hepta).

which are chlorine substitution products of cyclohexane, can be considered to consist in the difference of situation of chlorine and hydrogen atoms in the chair-form cyclohexane ring. As the possible configuration of chlorine and hydrogen atoms of BHC, hepta, and octa, theoretically speaking, thirteen, twenty, and twenty nine geometrical isomers respectively can exist, as shown in Fig. 2, 3, and 4.

For the representation of the models of these isomers the authors used the modifications of *Y. Morino's*<sup>(15)</sup> in which the cyclohexane ring is represented by a hexagonal ring, the chlorine atom in an equatorial bond (e)

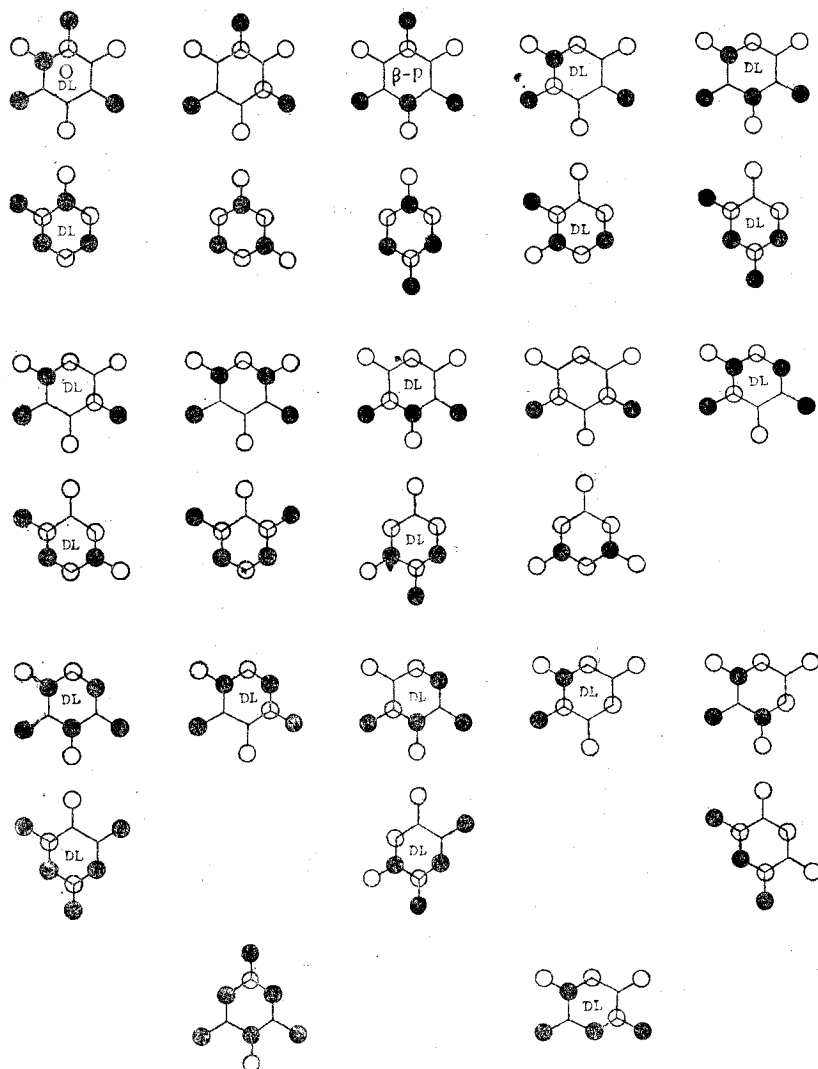


Fig. 4 : Geometrical Configuration of the Isomers of Dichlorobenzene Hexachloride (octa).

by a small circle connected with a short line, the chlorine atom in a polar bond (p) by a small circle on the hexagonal ring, and white and black circles represent chlorine atoms above and under the central plane.

The forms which are tagged "DL" can have optical isomers, and when they are taken into consideration, the theoretical isomers total sixteen, thirty two, and forty seven. These are the numbers of stereoisomers which can exist theoretically, but the actual numbers are much less on account of the repulsion among the atoms, chiefly among the chlorine atoms. The number of isomers of BHC, hepta, and octa reported so far are six, ten, and four respectively, as shown in Table 1.

Table 1: The Isomers of BHC, 1, 1, 2, 3, 4, 5, 6-Heptachlorocyclohexane and Dichlorobenzene Hexachloride.

Isomer		mp.	Discoverer
BHC $C_6H_6Cl_6$	$\alpha$	157~158°	Meunier (1887) <sup>(42)</sup>
	L- $\alpha$	128~132°	Cristol (1949) <sup>(27)</sup>
	$\beta$	310°, Sub.	Meunier (1887) <sup>(42)</sup>
	$\gamma$	112~113°	van der Linden (1912) <sup>(56)</sup>
	$\delta$	138~139°	"
	$\epsilon$	218.5~219.5°	Kauer (1947) <sup>(14)</sup>
1,1,2,3,4,5,6- Heptachloro- cyclohexane (hepta) $C_6H_5Cl_7$	$\alpha+$	153~154°	Matthews (1892) <sup>(44)</sup>
	$\beta++$	260°	"
	$\gamma$	85~86°	Ramsey (1946) <sup>(45)</sup>
	$\delta$	139~140°	Nakazima (1950) <sup>(25)</sup>
	$\delta'++$	156~157°	Scheuing (1950) <sup>(46)</sup>
	$\epsilon$	55~55.5°	Oiwa <sup>(31)</sup> , Nakazima <sup>(25)</sup> (1950)
	L- $\epsilon$	54~55°	Oiwa (1950) <sup>(31)</sup>
	$\epsilon'++$	96°	Coutier (1951) <sup>(28)</sup>
	$\zeta$	39°	"
	$\eta$	148°	"
Dichloro- benzene Hexachloride (octa) $C_6H_4Cl_8$	$\alpha$	149~150°	van der Linden (1912) <sup>(47)</sup>
	$\alpha$ -p	87°	"
	$\beta$ -p	265~266°	"
	m	81.8°	"

+ By the reasons stated in this text, the so-called  $\alpha$ -hepta in this report is an isomer of hepta with a melting point of 153~154°, and a half wave potential of about -0.94v. and a dipole moment of 1.19D.<sup>(18)</sup> The infrared absorption spectrum of this compound is measured by K. Kuratani.<sup>(49)</sup>

++ By the reasons stated in this text, the authors presume that  $\beta$ -hepta does not exist.

+++ Those marked with (') and those without them, though different, have been given the same symbol ( $\epsilon$ -, and  $\delta$ -), accidentally by their respective discoverers. The authors, therefore, have thus classified them for convenience sake.

For determining organic chemically the molecular configurations of these isomers, there are such ways as the decomposition reaction method, the synthetic reaction method and the separation of the optical active form, etc. However, if the decomposition reaction is used, which so often has been a means of determining the structures in the field of organic chemistry, the chair-form structure of the cyclohexane ring will be broken. This, as a result, makes the matter extremely complicated, so that the authors decided to take up a reaction which will not break the chair-form structures of these isomers. In this sense, these isomers were chlorinated under a suitable condition, wherein there is a possibility that the isomers will become higher chlorides having the same chair-form structure.

On the other hand, before the authors began their studies of BHC and their related compounds, the structure of  $\beta$ -BHC had been determined as shown in II of Fig. 2, from the standpoint of X-ray analysis by *R.D. Dickinson* and *C. Bilike*<sup>(5)</sup>, which was later supported by the studies of dipole moments<sup>(11,12)</sup>, and of electron diffraction measurement<sup>(22)</sup>, and there remains no room for argument. The authors believed that it is possible to determine the structures in question inductively after relating the compounds shown in Table 1 directly or indirectly with  $\beta$ -BHC, with the medium of the products of the above mentioned chlorination.

## II. Chlorination of the Isomers of BHC, hepta, Mono-, and Dichlorobenzene

The authors chlorinated the isomers of BHC, hepta, monochlorobenzene, and o-, and p-dichlorobenzene, and with the supplement of polarographic analysis and in part, regarding  $\alpha$ -BHC, of infrared analysis, separated the products by partition chromatography or recrystallization. The starting compounds and the chlorination products identified are shown in Table 2. The reactions in Table 2 are illustrated in Fig. 5, and 6.

Among these,  $\epsilon$ -hepta obtained by the chlorination of  $\gamma$ -, and  $\alpha$ -BHC, and monochlorobenzene, is a new isomer of hepta with the melting point of 55~55.5°, the half wave potential\* of about -0.9v., and the dipole moment of 2.22D. This was identified from its chlorine contents, from the fact that when it is dehydrochlorinated by alkali it produces 1,2,3,5-tetrachlorobenzene with 1,2,3,4,5,6-hexachlorocyclohexene having the melting point of 100~101°, and from the fact that it can also be produced by the chlorination of monochlorobenzene. When  $\epsilon$ -hepta was reacted with L-brucine in dioxane, the optical active form of  $\epsilon$ -hepta was separated of which the melting point was 54~55°, and the specific rotation was -21.6°. Consequently, the original  $\epsilon$ -hepta should be a DL-compound.

Now, the authors wish to compare the results thus obtained with the re-

\*The half wave potential in this report is shown by N-Calomel Electorode Standard.

Table 2: The Compounds which are obtained from the Isomers of Monochlorobenzene, Dichlorobenzene, BHC and hepta by Chlorination.

React. No.	Starting Compound	Identification by Polarography	Isolated pure Compound
7, 11, 18	monochlorobenzene	$\alpha$ -, $\gamma$ -, and $\epsilon$ -hepta	$\alpha$ -, $\gamma$ -, and $\epsilon$ -hepta $\beta$ -p-octa
2	o-dichlorobenzene	o-octa	o-octa
15	p-dichlorobenzene	—	$\beta$ -p-octa
1,16	$\alpha$ -BHC	$\gamma$ -hepta o-octa nona*	$\gamma$ -, $\delta$ -, and $\epsilon$ -hepta o-octa
3, 5, 8	$\beta$ -BHC	$\alpha$ -hepta o-octa nona	$\alpha$ -hepta o-, and $\beta$ -p-octa
17	$\gamma$ -BHC	$\epsilon$ -hepta	$\epsilon$ -hepta
6, 10, 12	$\delta$ -BHC	$\alpha$ -, and $\gamma$ -hepta o-octa nona	$\alpha$ -hepta o-, and $\beta$ -p-octa
14	$\epsilon$ -BHC	nona	$\beta$ -p-octa
4, 13	$\alpha$ -hepta	o-octa nona	o-, and $\beta$ -p-octa
9	$\gamma$ -hepta	o-octa nona	o-octa

\* nona (trichlorobenzene hexachloride).

sults of the various investigations. By *F.E. Matthews*<sup>(49)</sup>,  $\alpha$ -hepta (I) with a melting point of about 145° and  $\beta$ -hepta with a melting point of 260° were obtained after chlorinating monochlorobenzene. Recently, however, it was reported by *M. Nakazima et al.*<sup>(50)</sup> that  $\alpha$ -hepta (II) with a melting point of 153~154° and  $\beta$ -hepta with a melting point of 260° were obtained after chlorinating monochlorobenzene, and (II) was purified several times, but its melting point always showed 153~154°. Next, it was reported by *N. Tanaka et al.*<sup>(51)</sup> that an isomer of hepta with a melting point of about 155° was obtained after chlorinating monochlorobenzene by Matthews' method, and this isomer was the same as (I), and because of the incomplete purification, in the case of Matthews' experiments, it was supposed that (I) had showed a low melting point. The authors also chlorinated monochlorobenzene under almost the same conditions as above, and it was made clear that (I) was not obtained but (II) was obtained with  $\gamma$ -, and  $\epsilon$ -hepta, and the yield of (II) was larger than that of  $\gamma$ -, or  $\epsilon$ -hepta. From these results the authors supported the standpoint that the melting point of  $\alpha$ -hepta is 153~154° or about 155°. By these reasons, if the melting point of  $\alpha$ -hepta is 153~154°, there is a possibility that the isomer of hepta with a mel-

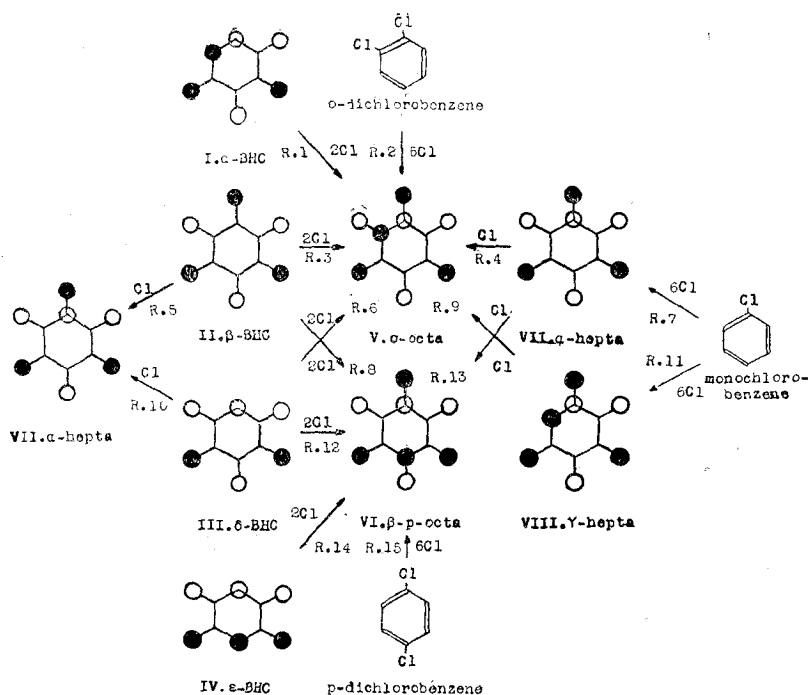


Fig. 5: Chlorination of the isomers of BHC, hepta, Dichlorobenzene, and Monochlorobenzene.

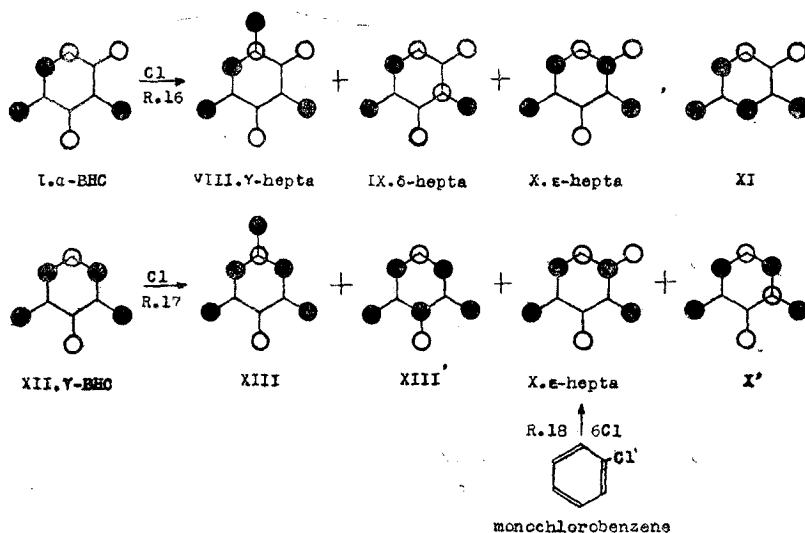


Fig. 6: Chlorination of α- and γ-BHC, and Monochlorobenzene.

ting point of 156~157° (δ'-) which was obtained with γ-hepta from the technical BHC products by G. Scheuing<sup>(46)</sup>, is the same as (II). The authors wish to discuss later on the isolation of β-hepta. Next, o-, and p-dichlorobenzene were chlorinated by the same method as van der Linden's, and



the results agreed with those obtained by him<sup>(47)</sup>. By van der Linden<sup>(24)</sup>, 1,1,2,2,3,4,4,5,6-nonachlorocyclohexane was obtained after chlorinating  $\alpha$ -BHC, and  $\beta$ -p-octa was obtained by chlorinating  $\beta$ -BHC. These results agree with that of the authors. Moreover, by *M.L.Coutier*<sup>(28)</sup>,  $\gamma$ -hepta (III) with a melting point of 84° and a small quantity of  $\zeta$ -hepta (IV) with a melting point of 39° were obtained after chlorinating  $\alpha$ -BHC, and  $\beta$ -hepta was obtained after chlorinating  $\beta$ -BHC, and (IV) was obtained after chlorinating  $\gamma$ -BHC, and  $\beta$ -,  $\gamma$ -, and  $\alpha$ -hepta (V) with a melting point of 143° were obtained after chlorinating  $\delta$ -BHC and  $\epsilon$ '-hepta with a melting point of 96° and  $\eta$ -hepta with a melting point of 148° were obtained after chlorinating  $\epsilon$ -BHC. This report is rather difficult to follow as the details of the experiments are not mentioned. Among these, the result that (III) was obtained from both  $\alpha$ -, and  $\delta$ -hepta, agree with the authors' results. However, the melting point of (V) obtained from  $\delta$ -hepta is lower than (II), but the authors suppose that the melting point will rise by further recrystallization. The melting point of (IV) is lower than that of  $\epsilon$ -hepta with a melting point of 55~55.5° obtained from both  $\alpha$ -, and  $\gamma$ -BHC by the authors. However, as described later, the possible geometrical isomers of hepta which can be obtained from  $\alpha$ -, and  $\gamma$ -BHC is only one, so that the authors suppose that the melting point of (IV) will rise if recrystallization is further repeated. Moreover, as  $\beta$ -hepta was obtained from monochlorobenzene and  $\beta$ -, and  $\delta$ -BHC by Matthews, *Nakazima*, and Coutier respectively, the authors also supposed at first that the substance with a melting point of 265~266° obtained by the chlorination of monochlorobenzene,  $\beta$ -, and  $\delta$ -BHC respectively, was  $\beta$ -hepta. However, further investigations showed, contrary to their presumption, that they were all  $\beta$ -p-octa. It is supposed that the so-called  $\beta$ -hepta which was obtained by Matthews, *Nakazima*<sup>\*\*</sup>, and Coutier was probably a mistake of  $\beta$ -p-octa which was produced by more chlorine substitution of  $\alpha$ -hepta produced. This carries a great influence upon the determination of structures which will be mentioned later.

### III. The Assignment of the Molecular Configuration of the Isomers of BHC, hepta, and octa

The molecular structure of  $\beta$ -BHC has already been determined as shown in II of Fig. 5 as stated above. Consequently, the structure of  $\alpha$ -hepta is determined from React. 5, and 7 as in VII, of o-octa from React. 2, and 3 as in V, and of  $\beta$ -p-octa from React. 8, and 15 as in VI. Among the thirteen geometrical isomers of BHC, I, and III are the only structures which can produce o-octa, besides II. Experimentally, besides  $\beta$ -BHC,  $\alpha$ -, and  $\delta$ -BHC

<sup>\*\*</sup>Afterwards, *Nakazima* et al. (unpublished) arrived at the same view as that of the authors.

could produce o-octa. Therefore either I or III must be  $\alpha$ -BHC, and the rest  $\delta$ -BHC. Of these two structures, III can produce  $\alpha$ -hepta, and I cannot. Experimentally,  $\alpha$ -hepta was produced from  $\delta$ -BHC. The conclusion is, therefore, that III is the molecular configuration of  $\delta$ -BHC, and I of  $\alpha$ -BHC. Among the thirteen geometrical isomers of BHC, the structures which can produce  $\beta$ -p-octa are II, III, and IV, but two of these are  $\beta$ -BHC, and  $\delta$ -BHC. Experimentally, from  $\epsilon$ -BHC,  $\beta$ -p-octa was also produced. As a result, IV must be the structure of  $\epsilon$ -BHC. Among the twenty geometrical isomers of hepta, the structures which can produce o-octa of V are VII and VIII, but VII is the structure of  $\alpha$ -hepta. As o-octa was also produced from  $\gamma$ -hepta experimentally, VIII must be the structure of  $\gamma$ -hepta.

The possible geometrical isomers of hepta, which can be derived from  $\alpha$ -BHC of I are VIII, IX, and X of Fig. 6. Since VIII is  $\gamma$ -hepta, one of the two forms left is of  $\delta$ -hepta, and the other of  $\epsilon$ -hepta. Now, taking into account the fact that the forms IX and X can also be derived from the forms XI, and XII of the thirteen geometrical isomers of BHC respectively, and that the experimental result that  $\epsilon$ -hepta is also produced by the chlorination of  $\gamma$ -BHC, it must be considered that one of the two, XI or XII, is the molecular configuration of  $\gamma$ -BHC. As has been pointed out by Y. Morino, I. Miyagawa, and T. Oiwa<sup>(13)</sup> the calculated values of the dipole moments of the two forms are 1.88D(XI) and 3.19~2.93D(XII), and the experimental value for  $\gamma$ -BHC is 2.80D. Consequently, XII should be the molecular configuration of  $\gamma$ -BHC. The possible geometrical isomers of hepta which can be derived from XII are XIII, XIII', X, and X', but among them only X can be obtained by the chlorination of both  $\alpha$ -, and  $\gamma$ -BHC. It is proved, therefore, that X is  $\epsilon$ -hepta and IX is  $\delta$ -hepta. Moreover D-, and L-forms are possible for X and this agrees completely with the experimental result that the optical active form of  $\epsilon$ -hepta was separated.

It is interesting that the structures determined here are stabler forms with little repulsion among the chlorine atoms, and that the isomers which possess the center of symmetry have higher melting points and less solubilities, and are slow to be dehydrochlorinated by alkali and hard to be chlorinated.

Now, the authors wish to compare the structures thus determined, with the results of the various investigators. The structure of  $\alpha$ -BHC determined here agrees completely with the presumptions by R.E. Slade<sup>(3)</sup>, and S.J. Cristol<sup>(27)</sup>, the conclusions of the electron diffraction measurement by O. Bastiansen et al.<sup>(28)</sup>, and of the dipole moment measurement by Y. Morino et al.<sup>(15)</sup> The structure of  $\gamma$ -BHC differs from the presumptions by R.E. Slade<sup>(3)</sup>, and others<sup>(16,52,57)</sup>, but agrees with the conclusions of X-ray analysis by van Vloten et al.<sup>(6,7)</sup>, of the electron diffraction measurement by O. Bastiansen et al.<sup>(28)</sup>, of the

dipole moment measurement by *Y. Morino* et al.<sup>(18)</sup>, and of the dehydrochloration of  $\gamma$ -BHC and the chlorination of the dehydrochlorinated products by *M. Nakazima* et al.<sup>(25,26)</sup> The structure of  $\delta$ -BHC differs from the one with the center of symmetry presumed by *R.S. Slade*<sup>(3)</sup> and others<sup>(16,52,57)</sup>, but agrees with the conclusions of electron diffraction measurement by *O. Bastiansen* et al.<sup>(23)</sup>, of X-ray analysis by *A.J. van Bommel* et al.<sup>(8)</sup>, of dipole moment measurement by *Y. Morino* et al.<sup>(18)</sup>, and of dehydrochlorination of  $\delta$ -BHC and chlorination of its products by *M. Nakazima* et al.<sup>(25)</sup> The structure of  $\epsilon$ -BHC differs from the presumption of *R.E. Slade*<sup>(3)</sup> and others<sup>(16,52,57)</sup>, but agrees with the conclusions of dipole moment measurements by *E. Hetland*<sup>(15)</sup> and *Y. Morino* et al.<sup>(18)</sup>, of electron diffraction measurement by *O. Bastiansen* et al.<sup>(23)</sup>, and of X-ray analysis by *N. Norman*<sup>(19)</sup>. The structures of  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -hepta agree with the proposition by *M. Nakazima* et al.<sup>(25,26)</sup>, and do not conflict with the results of the dipole moment by *Y. Morino* et al.<sup>(18)</sup>, but differ from the molecular configuration from the standpoint of chlorination reaction by *M.L. Coutier* et al.<sup>(28)</sup> in which the cyclohexane ring is assumed to be hexagonal plane. The structure of  $\beta$ -p-octa agrees with the molecular configuration from the standpoint of chlorination reaction by van der Linden<sup>(24)</sup>, in which the cyclohexane ring is assumed to be a hexagonal plane, and do not conflict with the results of the chlorination reaction of cyclohexane by *O. Hassel* et al.<sup>(29)</sup> The structures of  $\alpha$ -, and  $\beta$ -p-octa agree with the results of the dipole moment investigations by *Y. Morino* et al.<sup>(18)</sup>

## EXPERIMENTAL

### I. The Apparatus of the Chlorination Reaction

The apparatus of the chlorination reaction used in experiments (3), (4), (5), (6), (7), (8), and (10) was as follows:

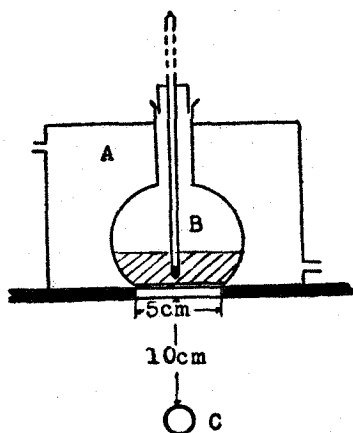


Fig. 7 : Apparatus of the Chlorination.

Inside thermostat (A) with a quartz window on the bottom, a 500cc quartz flask(B) with a flat bottom was placed. At ten centimeters below this thermostat, the direct-current, low pressure mercury arc-lamp(C) operated on 18v. and 3 amp. was placed. The groups of lines longer than  $3126\text{\AA}$  were used by filtering with glass filter.

### II. Polarographic Analysis, and Partition Chromatography

Polarographic analysis\*\*\* was used as the supplement to the organic chemical procedures. Experimental condition of the polarographic

analysis was nearly the same as in the case by *M.Suzuki* and *M.Nakazima*<sup>(53)</sup>, and is as follows:

Base solution: dioxane (40%), and 7.7%  $(\text{CH}_3)_4\text{NBr}$  solution (10%), and Koltoff's Buffer solution (pH=7), containing some gelatin as maximum suppressor (50%). Before recording, dissolved oxygen is removed from solution by a stream of hydrogen.

Recording range:  $-0.1 \sim -2.0\text{v.}$  (N-calomel electrode standard)

Temperature:  $25^\circ \pm 0.1^\circ$

Galvanometer sensitivity:  $3.09 \times 10^{-8}$  A/mm/m

Partition chromatography used was a modification of *L.L.Ramsey's* and *W.I.Patterson's*<sup>(45)</sup>, and was as follows:

Preparation of the partition chromatographic column: to 100g. of silicic acid (the size\*\*\*\* of these particles was about  $20 \sim 30\text{m}\mu$ ) in a large mixing vessel, 10g. of nitromethane was added five times, and mixed thoroughly after each addition. Then about 100g. of petroleum ether, bp  $60 \sim 80^\circ$ , was added six times, and mixed thoroughly until it became a slurry. The resultant slurry was poured into a glass tube (absorption tube). The size of this tube was 3 cm O.D.  $\times$  70 cm long and the constricted end was plugged with a small piece of cotton wool, and on it a small perforated plate about 2.8 cm in diameter was placed. The tube was placed in a clamp on a ring stand and connected to a compressor air line through the pressure regulator and pressure was applied. When there was sufficient space in the tube, the rest of the slurry was poured in. When the silicic acid was so firm that it retained its shape on tipping, the pressure was released.

Procedure of separation: The sample was dissolved in the petroleum ether reagent which was saturated with nitromethane. This solution was transferred to the absorption column, carefully so that the top of the silicic acid was not disturbed. The pressure line was connected to the column and sufficient pressure (3~7 lbs. per square inch) was applied to cause the solvent to perco-

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\*\*\*Of the five isomers of BHC, ten of hepta, four of octa;  $\gamma$ -BHC,  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -hepta and o-octa are reduced at a dropping mercury cathode and the half wave potentials of these compounds are about  $-1.15\text{v.}$ <sup>(53)</sup>,  $-0.94\text{v.}$ <sup>(51)</sup>,  $-0.8\text{v.}$ <sup>(51)</sup>,  $-0.95\text{v.}$ ,  $-0.9\text{v.}$ , and  $-0.25\text{v.}$ <sup>(54)</sup>, respectively. There are slight differences among these potentials, and also the forms of the waves of these compounds are rather different from one another. By comparing these potentials, it is known that the half wave potentials of the chlorine derivatives of cyclohexane decreases as their chlorine content increases.

The conclusion based only on polarographic analysis often lacks accuracy, because half wave potentials of the compounds mentioned above, especially of hepta, are very close with one another, and there is possible existence of unknown derivatives of which the half wave potentials are close to those of the above compounds. Therefore, the infra-red absorption analysis was used to trace these compounds in chlorination products of  $\alpha$ -BHC qualitatively.

\*\*\*\*This was measured by electron microscope by Mr. *M. Arakawa* of this Institute, to whom the authors' thanks are due.

late through the column at the rate of about 5cc per minute. The instant all the solution had sunk into the gel, the pressure was released. Then the tube was filled with the petroleum ether reagent and the pressure was applied again. After a certain volume of percolated solution had passed through the column, the collection of 20 cc fraction was begun, and the solvent was removed. The fractions were collected until no significant amount of material came through the column.

### III. Chlorination Reaction\*\*\*\*\*

#### (1). Chlorination of o-Dichlorobenzene(React. 2 of Fig. 5)

Forty milliliter of 1.5% NaOH solution was added to 40g. of o-dichlorobenzene

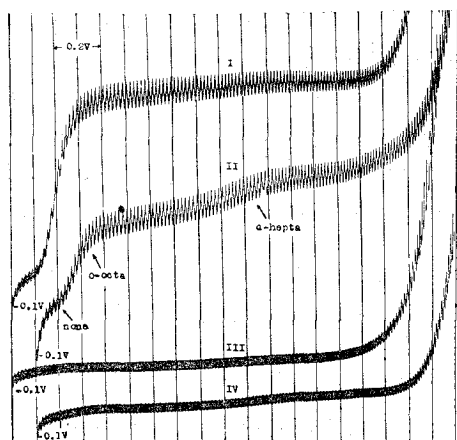


Fig. 8 : Polarogram(1).

- I. o-octa, conc.:  $4 \times 10^{-4}$ mol
- II. chlorination product of  $\beta$ -BHC.
- III.  $\beta$ -BHC, conc.:  $4 \times 10^{-4}$ mol
- VI.  $\beta$ -p-octa, conc.:  $4 \times 10^{-4}$ mol

zene(bp.179°; synthesized from o-chloroaniline by *Sandmeyer's* reaction<sup>(58)</sup>) in a flask, then the vessel was cooled by ice water, and chlorine was applied slowly for a period of two hours with strong stirring in the sun. The crystals produced were collected by filtration and recrystallized from isopropyl alcohol and methyl alcohol. Eighteen grams of crystals with a melting point 149~150° were obtained. The polarogram of this compound is shown in I of Fig.8, and the half wave potential of this compound was about -0.25v. The chlorine content was as follows:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No.1	21.2	67.9	79.06
	No.2	22.9	73.4	79.34
Calcd.		$C_6H_4Cl_8$ .....		78.88

Half a gram of these crystals were heated in 2.5N-NaOH methanolic solution for 10 minutes and 0.28g. of the crystals with a melting point of 85~85° were obtained. The chlorine analysis of this compound was as follows:

\*\*\*\*\*The dipole moment and the infrared absorption spectrum of each of the isomers of BHC, hepta and octa which were either used in, or produced by this chlorination were measured by *Y.Morino* et al.<sup>(18)</sup> and *K.Kuratani*<sup>(49)</sup> respectively.

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No. 1	22.4	63.8	70.49
	No. 2	23.2	65.9	70.30
Calcd.		C <sub>6</sub> HCl <sub>5</sub> .....		70.86

This compound did not show the depression of the melting point when mixed with pentachlorobenzene synthesized from 1,2,4-trichlorobenzene. This 1,2,4-trichlorobenzene was synthesized from p-dichlorobenzene by Diazo-reaction and *Sandmeyer's* reaction.<sup>(55)</sup>

From the above results, it was known that the crystals with a melting point of 149~150° are o-octa.

## (2). Chlorination of p-Dichlorobenzene(React. 15 of Fig. 5)

Thirty grams of p-dichlorobenzene (mp.54°) was dissolved into carbon tetrachloride and 150cc of 1.5% NaOH solution was added and chlorine gas transmitted with strong stirring in the sun. After about 2 hours, the crystals precipitated were collected by filtration and recrystallized from acetone. Eleven grams of crystals with a melting point of 265~266° were obtained. The polarogram of this compound is shown in IV of Fig. 8. The chlorine analysis gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No. 1	21.8	69.6	79.03
	No. 2	23.1	73.4	78.66
Calcd.		C <sub>6</sub> H <sub>4</sub> Cl <sub>5</sub> .....		78.88

Half a gram of these crystals were heated in 2.5N-NaOH methanolic solution for 10 minutes, and 0.30g. of the crystals with a melting point of 85~86° were obtained. The chlorine analysis of these crystals gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No. 1	22.6	64.9	71.06
	No. 2	22.5	64.1	70.49
Calcd.		C <sub>6</sub> HCl <sub>5</sub> .....		70.86

This compound did not show the depression of the melting point when mixed with pentachlorobenzene synthesized from 1,2,4-trichlorobenzene.

From the above results, the crystals having the melting point of 265~266° were identified to be β-p-octa.

## (3). Chlorination of β-BHC(React. 3, 5, and 8 of Fig. 5)

Two grams of β-BHC(mp.310°, Sub.) was photochlorinated in 150 g. of carbontetrachloride solution containing 6g. of chlorine at 40° for a period of one hour. The polarogram of the β-BHC is shown in III of Fig.8. As soon as the reaction was finished the solvent was removed by distillation on steam

bath in the dark, and then by strong steam distillation 2.32g. of yellowish solid was obtained. The polarogram of this solid is shown in II of Fig. 8, and it was assumed that about 9% of  $\alpha$ -hepta and about 24% of o-octa and nona existed. This solid was dissolved into 30cc petroleum ether, and insoluble matter(I) and solution(II) were separated. (I) was recrystallized from isopropyl alcohol and methyl alcohol and 0.22g. of crystals(III) with a melting point of 265~266° and 0.1g. of unreacted  $\beta$ -BHC was obtained. (II) was separated by partition chromatography and the crystals separated were recrystallized from isopropyl alcohol. Zero point zero four gram of crystals(IV) with a melting point of 153~154°, and 0.11g. of crystals(V) with a melting point of 149~150° were obtained. Crystals (III), (IV), and (V) did not show the depression of the melting point when mixed with  $\beta$ -p-octa,  $\alpha$ -hepta, and o-octa, respectively.

#### (4). Chlorination of $\delta$ -BHC(React. 6, 10, and 12 of Fig. 5)

In exactly the same way as in the case of  $\beta$ -BHC, 2g. of  $\delta$ -BHC(mp.138~139°) were photochlorinated and 2.42g. of yellowish solid was obtained. The polarogram of the  $\delta$ -BHC is shown in III of Fig.9, and the polarogram of

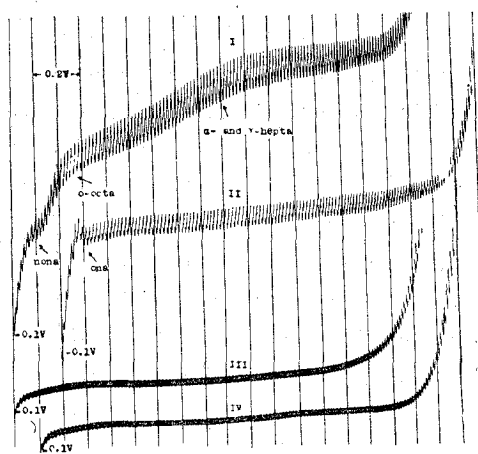


Fig. 9 : Polarogram(2).

- I. chlorination product of  $\delta$ -BHC
- II. chlorination product of  $\epsilon$ -BHC
- III.  $\delta$ -BHC, conc.:  $10^{-4}$ mol
- VI.  $\epsilon$ -BHC, conc.:  $10^{-4}$ mol

this solid is shown in I of Fig. 9, and it was assumed that  $\alpha$ -, and  $\gamma$ -hepta and 30% of o-octa existed. This solid was dissolved into 30cc petroleum ether, and insoluble matter(I) and solution(II) were separated. (I) was recrystallized from isopropyl alcohol and methyl alcohol, and 0.32g. of crystals(III) with a melting point of 262~264° were obtained. (II) was separated by partition chromatography and the crystals separated were recrystallized from isopropyl alcohol. Zero point zero six gram of crystals(IV) with a melting point of 153~154° and 0.15g. of crystals(V) with a melting point of 149~150° were obtained. Crystals (III),

(IV), and (V) did not show the depression of the melting point when mixed with  $\beta$ -p-octa,  $\alpha$ -hepta, and o-octa, respectively.

#### (5). Chlorination of $\epsilon$ -BHC (React. 14 of Fig. 5)

In exactly the same way as in the case of  $\beta$ -BHC, 0.3g. of  $\epsilon$ -BHC† (mp.217~218°) was photochlorinated and 0.35g. of yellowish solid was obtained. The

†This  $\epsilon$ -hepta was presented to the authors by Dr. K.C.Kauer of Dow Chem. Co.

polarogram of the  $\epsilon$ -BHC is shown in IV of Fig. 9, and the polarogram of this solid is shown in II of Fig. 9, and it was proved that there were no  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -hepta, nor o-octa, but there was nona. This solid was recrystallized from isopropyl alcohol and methyl alcohol, and 0.082g. of crystals(I) with a melting point of  $262^\circ$  and unreacted  $\epsilon$ -BHC were obtained. Crystals(I) did not show the depression of the melting point when mixed with  $\beta$ -p-octa.

#### (6). Chlorination of $\alpha$ -hepta (React. 4, and 13 of Fig. 5)

In exactly the same way as in the case of  $\beta$ -BHC, 2g. of  $\alpha$ -hepta( $153\sim 154^\circ$ ), which was obtained from monochlorobenzene, was photochlorinated, and 2.08g. of yellowish solid was obtained. The polarogram of the  $\alpha$ -hepta is shown in II of Fig. 10, and the polarogram of this solid is shown in I of Fig. 10, and it was

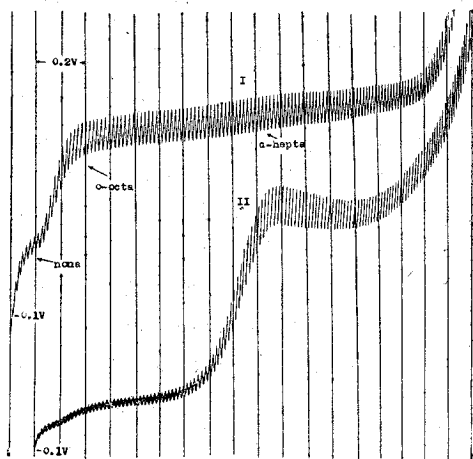


Fig. 10 : Polarogram(8).

- I. chlorination product of  $\alpha$ -hepta
- II.  $\alpha$ -hepta, conc.:  $7 \times 10^{-4}$ mol

assumed that there were about 30% of o-octa, nona, and unreacted  $\alpha$ -hepta. This solid was dissolved into 30cc petroleum ether, and insoluble matter (I) and solution (II) were separated. (I) was recrystallized from isopropyl alcohol and methyl alcohol, and 0.12g. of crystals (III) with a melting point of  $262^\circ$  were obtained. (II) was separated by partition chromatography and the crystals separated were recrystallized from isopropyl alcohol. Zero point one two gram of crystals(IV) with a melting point of  $149\sim 150^\circ$  were obtained. Crystals(III) and (IV)

did not show the depression of the melting point when mixed with  $\beta$ -p-octa, and o-octa, respectively.

#### (7). Chlorination of $\gamma$ -hepta (React. 9 of Fig. 5)

In exactly the same way as in the case of  $\beta$ -BHC, 2g. of  $\gamma$ -hepta(mp. $85\sim 86^\circ$ ), which was obtained from monochlorobenzene, was photochlorinated, and 2.16g. of yellowish oily substance was obtained. The polarogram of the  $\gamma$ -hepta is shown in II of Fig. 11, and the polarogram of this oily substance is shown in I of Fig. 11, and it was assumed that there were about 30% of o-octa, nona, and unreacted  $\gamma$ -hepta. This substance was separated by partition chromatography and the crystals separated were recrystallized from isopropyl alcohol. Zero point one five gram of crystals(I) with a melting point of  $149\sim 150^\circ$  were obtained. Crystals(I) did not show the depression of the melting point when mixed with o-octa.



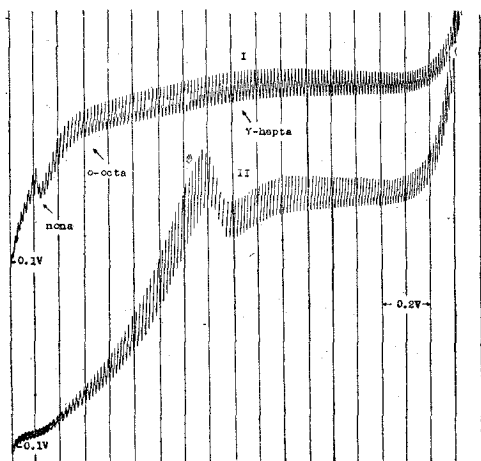


Fig. 11 : Polarogram(4).

- I. chlorination product of  $\gamma$ -hepta
- II.  $\gamma$ -hepta, conc.:  $4 \times 10^{-4}$  mol

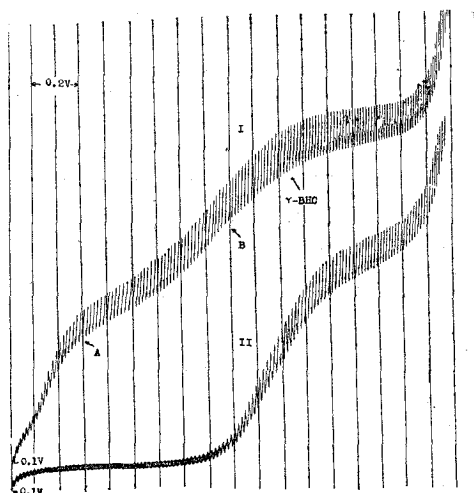


Fig. 12 : Polarogram(5).

- I. chlorination product of  $\gamma$ -BHC
- II.  $\gamma$ -BHC, conc.:  $4 \times 10^{-4}$  mol

#### (8). Chlorination of $\gamma$ -BHC (React. 17 of Fig. 6)

Thirteen grams of  $\gamma$ -BHC (mp.  $112 \sim 113^\circ$ ) was photochlorinated in 400g. of carbontetrachloride solution containing 16g. of chlorine, at  $40^\circ$  for a period of 1.5 hours. As soon as the reaction was finished, by distillation on the steam bath and then under diminished pressure, the solvent was removed. Finally 18g. of the residual oily substance was obtained. The polarogram of the  $\gamma$ -BHC is shown in II of Fig. 12, and the polarogram of this substance is shown in I of Fig. 12. By observing this polarogram, it was found that  $\gamma$ -BHC was changed into at least two of the more chlorinated compounds, e.g. A and B. Five grams of this oily substance was dissolved in 40cc petroleum ether and transferred into partition column. The result of the separation is shown collectively in Table 3. After repeating nine times the same procedure with 46g. of other oily substance, the fractions corresponding to the fractions No. 7, 8, 9, and 10 were combined into one, and 12.7g. of rough crystals with a melting range of  $45 \sim 49^\circ$  were obtained. These crystals were refractionated in a fresh column of the same size, and the middle fractions were collected and recrystallized from isopropyl alcohol. Thus 7.6g. of crystals were obtained of which the melting point was  $55 \sim 55.5^\circ$ , and the half wave potential was about  $-0.9v.$ , and the dipole moment was 2.20D.<sup>††</sup> The polarogram of this compound is shown in II of Fig. 13, and the elementary analysis gave the following results:

<sup>††</sup>This dipole moment was measured by Prof. Y. Morino and Mr. I. Miyagawa,<sup>(45)</sup> Chemical Laboratory, Faculty of Science, Tokyo University.

Table. 3: Illustrating the Collection of Percolate Fractions and their Classification from one Chlorination Product of  $\gamma$ -BHC (5.1 g. of petroleum ether soluble material placed on the column).

Fraction		Description	Classification
No. *	Weight g.		
1	0.21	oil; slightly colored	unknown
2	0.28	"	"
3	0.36	"	"
4	0.34	"	octa
5	0.37	"	"
6	0.39	"	a mixture of octa, and hepta
7	0.34	crystals containing some oil; colorless	a mixture of hepta, and a little octa
8	0.38	"	hepta
9	0.29	"	"
10	0.31	"	"
11	0.32	oil; slightly colored	a mixture of hepta, and $\gamma$ -BHC
12	0.33	oily solid; colorless	"
13-16	1.12	crystals; colorless	$\gamma$ -BHC

\* 20cc fraction, No. 1 being 120-140cc fraction.

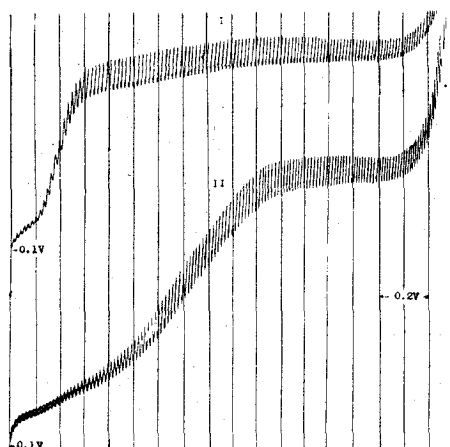


Fig. 13 : Polarogram(6).

- I. 1,2,3,4,5,6-hexachlorocyclohexene  
(mp.100~101°), conc.:  $4 \times 10^{-4}$ mol  
II.  $\epsilon$ -hepta, conc.:  $4 \times 10^{-4}$ mol

		Smple(mg.)	AgCl(mg.)	Cl%
Found	No. 1	21.3	65.6	76.25
	No. 2	22.6	69.8	76.46
Calcd.	C <sub>6</sub> H <sub>5</sub> Cl <sub>7</sub> .....			76.32

		Sample(mg.)	CO <sub>2</sub> (mg.)	H <sub>2</sub> O(mg.)	C%	H%
Found	No. 1	5.488	4.448	0.736	22.08	1.49
	No. 2	4.782	3.887	0.637	22.17	1.48
Calcd.	C <sub>6</sub> H <sub>5</sub> Cl <sub>7</sub> .....				22.14	1.54

Four hundred and fifty grams of acetone was placed in a flask and 3g. of the above mentioned crystals with a melting point of 55~55.5° were dissol-

ved in it. Five hundred and fifty milliliters of Koltoff's buffer solution of pH=10 was added slowly for a period of 30 minutes with continuous stirring, while the temperature of the reaction was held at 30° by means of a water thermostat. The reaction was then stopped by the addition of a certain amount of N-HCl solution. The acetone was removed by steam distillation and the residual mixture was extracted with ether. Thus 1.9g. of oily substance containing some crystals was obtained. This substance was dissolved in 20cc of the petroleum ether and transferred into partition column. The result of the separation is shown collectively in Table.4.

Table.4: Illustrating the Collection of Percolate Fractions and their Classification from one Dehydrochlorination Product of  $\epsilon$ -1, 1, 2, 3, 4, 5, 6-Heptachlorocyclohexane (1.9 g. of petroleum ether soluble material placed on the column).

Fraction		Description	Classification
No. *	Weight g.		
1	trace	oil; slightly colored	unknown
2	0.12	solid colorless	tetrachlorobenzene
3	0.16	"	a mixture of tetrachlorobenzene and a little hexachlorocyclohexene
4	0.24	solid; colorless	a mixture of tetrachlorobenzene and hexachlorocyclohexene
5	0.27	crystals; colorless	hexachlorocyclohexene
6	0.26	solid; colorless	a mixture of hexachlorocyclohexene and $\epsilon$ -hepta
7	0.24	oil; slightly colored	"
8	0.18	crystals; colorless	$\epsilon$ -hepta
9	0.13	"	"
10	0.06	oil; slightly colored	unknown
11	trace	"	"

\* 20cc fraction, No.1 being the 140-160cc fraction.

The fractions No. 2 (mp.40~43°), and 3(mp.30~32°) were combined and purified from isopropyl alcohol. Thus, 0.12 gram of crystals with a melting point of 48~49° were obtained. The chlorine analysis gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No. 1	19.7	52.3	65.40
	No. 2	21.3	56.8	66.00
Calcd.	C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub>			65.71

This compound did not show the depression of the melting point when mixed with 1, 2, 3, 5-tetrachlorobenzene synthesized from 1, 2, 4-trichlorobenzene.

The fractions No.4(mp.70~90°), and 5(mp.80~90°) were combined and recrystallized from isopropyl alcohol. Thus, 0.22g. of crystals were obtained of which the melting point was 100~101° and the half wave potential was about -0.3v. The polarogram of it is shown in I of Fig.13. The chlorine analysis gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No.1	22.4	66.3	73.21
	No.2	19.7	58.8	73.87
Calcd.		C <sub>6</sub> H <sub>4</sub> Cl <sub>6</sub>		73.68

This compound did not show the depression of the melting point when mixed with an isomer of 1,2,3,4,5,6-hexachlorocyclohexene of melting point 100~101° isolated recently by *M. Nakazima et al.*<sup>(25)</sup>, which showed therefore, the two compounds were the same.

From the above results, the authors believe that the above compound having the melting point of 55~55.5° is a new isomer of hepta and hereafter this compound is called ε-form.

(9). Chlorination of Monochlorobenzene (React. 7 and 11 of Fig. 5, and React. 18 of Fig. 6)

One hundred millilitres of 1% NaOH solution was added to 200g. of monochlorobenzene (bp.132°) in a flask, then the vessel was cooled by ice water, and chlorine was applied slowly for a period of 2 hours with strong stirring in the sun, while 100cc of 1% NaOH solution was dropped anew during the reaction. When the reaction was over, the oily substance was separated and about 50g. of unreacted monochlorobenzene was removed by distillation. After one night's cooling off, the produced crystals(I) were separated and the unreacted matter was removed at a diminished pressure. Thus, 203.5g. of oily substance was obtained. To this substance, 40cc of petroleum ether was added, and dissolved by heat, then cooled for one night, and the produced crystals(II) were separated from the mother liquid. This liquid was steam distilled, and 16.5g. of oily substance was obtained from the middle fraction. Ten millilitres of ethyl alcohol was added to this, cooled, and then the produced crystals(III) were separated. The mother liquid was refractionated by partition chromatography, and the crystals refractionated were recrystallized from isopropyl alcohol. Thus, 5.43g. of crystals(IV) with a melting point of 85~86° and having the half wave potential of about -0.8v. and 1.12g. of crystals(V) with a melting point of 55~55.5° and having the half wave potential of about -0.9v. were obtained.

The chlorine analysis of crystals(IV) gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No.1	27.6	85.4	76.58
	No.2	26.9	82.9	76.27
Calcd.		C <sub>6</sub> H <sub>5</sub> Cl <sub>7</sub>		76.32

Ten grams of crystals(IV) were heated in 1000cc of 0.1N-NaOH methanolic solution for 1.5 hours, and 6.1g. of solid with a melting range of 29~30° was

obtained. This solid was recrystallized from methyl and ethyl alcohol and 2.6g. of crystals with a melting point 31~33° were obtained. These crystals are a mixture of the isomers of tetrachlorobenzene and their elementary analysis gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%	
Found	No. 1	29.7	78.0	65.42	
	No. 2	28.6	75.7	65.94	
Calcd.		C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> .....		65.71	

		Sample(mg.)	CO <sub>2</sub> (mg.)	H <sub>2</sub> O(mg.)	C%	H%
Found	No. 1	4.962	5.988	0.411	32.91	0.92
	No. 2	5.132	6.185	0.434	32.87	0.94
Calcd.		C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> .....			33.35	0.93

From these results, it was known that crystals(IV) were  $\gamma$ -hepta.

Crystals(V) did not show the depression of the melting point when mixed with  $\epsilon$ -hepta obtained from  $\gamma$ -BHC.

Crystals(I), (II), and (III) were combined and recrystallized from ethyl alcohol and chloroform, and 21.9g. of crystals(VI) with a melting point of 153~154° and 19.7g. of crystals(VII) with a melting point of 265~266° were obtained. The polarogram of crystals(VI) is shown in II of Fig 10, and the half wave potential was about -0.94v. The chlorine analysis of crystals(VI) gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No. 1	23.9	73.9	76.52
	No. 2	24.6	76.3	76.74
Calcd.		C <sub>6</sub> H <sub>5</sub> Cl <sub>7</sub> .....		76.32

Ten grams of crystals (VI) were heated in 1000cc of 0.1N-NaOH methanolic solution for 1.5 hours and 6.4g. of solid with a melting range of 28~30° was obtained. This solid was recrystallized from methyl and ethyl alcohol and 2.2g. of crystals with a melting point of 31~33° were obtained. These crystals are a mixture of the isomers of tetrachlorobenzene and their elementary analysis gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%	
Found	No. 1	29.4	77.2	65.41	
	No. 2	28.3	74.8	65.83	
Calcd.		C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> .....		65.71	

		Sample(mg.)	CO <sub>2</sub> (mg.)	H <sub>2</sub> O(mg.)	C%	H%
Found	No. 1	5.401	6.616	0.442	33.41	0.91
	No. 2	5.203	6.355	0.440	33.31	0.94
Calcd.		C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub> .....			33.35	0.93

From these results, it was known that crystals(VI) were  $\alpha$ -hepta.

The polarogram of crystals (VII) was the same as IV of Fig. 8. The chl-

orine analysis gave the following results:

		Sample(mg.)	AgCl(mg.)	Cl%
Found	No. 1	20.9	65.7	78.32
	No. 2	23.7	74.5	78.31
Calcd.	$C_6H_4Cl_8$	.....78.88		

Half a gram of crystals(VII) were heated in 2.5N-NaOH methanolic solution for 10 minutes, and 0.29g. of the crystals with a melting point of  $85\sim 86^\circ$  were obtained. This compound did not show the depression of the melting point when mixed with pentachlorobenzene stated above. Moreover crystals (VII) did not show the depression of the melting point when mixed with  $\beta$ -p-octa obtained from p-dichlorobenzene.

(10). Chlorination of  $\alpha$ -BHC (React. 1 of Fig. 5, and React. 16 of Fig. 6)

In exactly the same way as in the case of  $\gamma$ -BHC, 13g. of  $\alpha$ -BHC (mp. $157\sim$

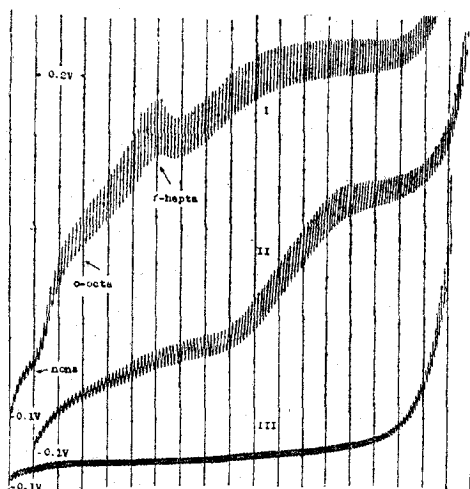


Fig. 14 : Polarogram(7).

- I. chlorination product of  $\alpha$ -BHC
- II.  $\delta$ -hepta, conc.:  $6 \times 10^{-4}$ mol
- III.  $\alpha$ -BHC , conc.:  $4 \times 10^{-4}$ mol

158 $^\circ$ ) was chlorinated and 17.8g. of oily substance was obtained. The polarogram of the  $\alpha$ -BHC is shown in III of Fig.14 and the polarogram of this substance is shown in I of Fig.14, and it was assumed that about 27% of o-octa,  $\gamma$ -hepta, and nona existed. Six point five grams of this substance was separated by partition chromatography, and the result is collectively shown in Table 5. Further, 95g. of the oily substance was separated in the same way. The fractions corresponding to fractions No.2,3, and 4 were combined into one and the crystals obtained were recrystallized from isopropyl

alcohol and methyl alcohol and 6.1 g. of crystals were obtained of which the melting point was  $149\sim 150^\circ$  and the half wave potential was about  $-0.25v$ . This compound did not show the depression of the melting point when mixed with o-octa.

The fractions corresponding to fractions No.6 and 7 were combined into one and the rough crystals obtained were recrystallized from isopropyl alcohol and methyl alcohol and 1.90g. of crystals were obtained, of which the melting point was  $85\sim 86^\circ$  and the half wave potential was about  $-0.8v$ . This compound did not show the depression of the melting point when mixed with  $\gamma$ -hepta which was synthesized from monochlorobenzene,

Table. 5: Illustrating the Collection of Percolate Fractions and their Classification from one Chlorination Product of  $\alpha$ -BHC (6.5 g. of petroleum ether soluble material placed on the column).

Fraction		Description	Classification
No. *	Weight g.		
1	0.31	crystals, containing some oil; colorless	a mixture of nona, and a little o-octa
2	0.42	crystals, containing some oil; colorless	a mixture of nona, and o-octa
3	0.40	"	a mixture of nona, and o-octa
4	0.46	"	a mixture of nona, o-octa, and $\gamma$ -hepta
5	0.49	oil; colorless	a mixture of nona, o-octa, and $\gamma$ -hepta
6	0.43	crystals; colorless	a mixture of $\gamma$ -hepta, and o-octa
7	0.44	crystals; slightly colored	a mixture of $\gamma$ -hepta, and a little o-octa
8	0.39	oil, containing some crystals; slightly colored	a mixture of $\alpha$ -BHC, and $\gamma$ -, and $\epsilon$ -hepta
9	0.44	"	"
10	0.47	solid, containing some oil; colorless	a mixture of $\alpha$ -BHC, and $\gamma$ -, and $\delta$ -hepta
11	0.40	solid, containing some oil; slightly colored	"
12	0.39	"	"
13-15	0.79	crystals; colorless	$\alpha$ -BHC

\* 20cc fraction, No. 1 being 120-140cc fraction.

The fractions corresponding to fractions No. 8 and 9 were combined into one and 13.41g. of oily substance was obtained. This substance was refractionated in the fresh column, and the middle fractions were collected. The infra-

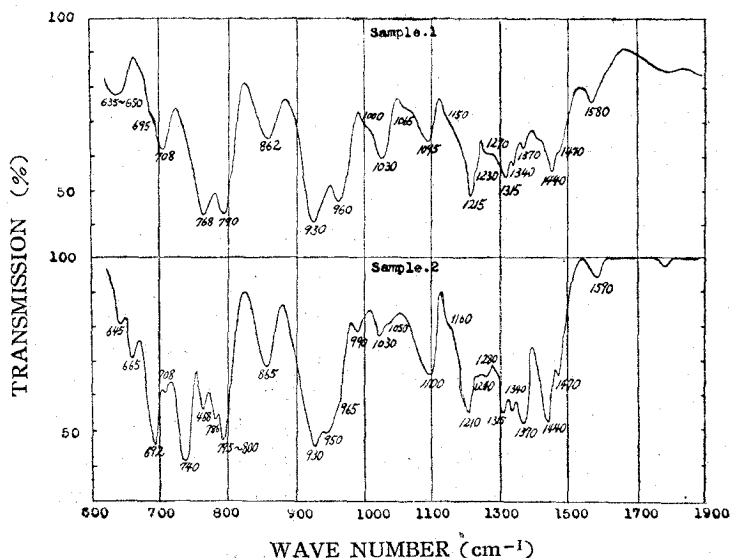


Fig. 15 : Infrared Absorption Spectra of Substance of Percolate Fractions.

red absorption spectrum††† of this substance is Sample. 2 of Fig.15. This curve shows the characteristic absorptions of  $\epsilon$ -hepta, besides  $\gamma$ -hepta, and consequently the existence of the considerable amount of  $\epsilon$ -hepta. The substance was refractionated in the fresh column, and the middle fractions were collected. Then the substance was fractionally recrystallized from isopropyl alcohol and 156g. of crystals were obtained of which the melting point was  $55\sim 55.5^\circ$  and the half wave potential was about  $-0.9v$ . This compound did not show the depression of the melting point when mixed with  $\epsilon$ -hepta which was obtained by chlorination of  $\gamma$ -BHC.

The fractions corresponding to fractions No.10, 11, and 12 were combined into one and 21.55g. of solid was obtained. This solid was refractionated in a fresh column and the middle fractions were collected and 13.96g. of solid was obtained. The infrared absorption spectrum††† of this substance is Sample. 1 of Fig.15. This curve shows, besides  $\gamma$ -hepta, the characteristic absorption of  $\delta$ -hepta, and consequently the existence of a small amount of  $\delta$ -hepta. The substance was refractionated three times in the fresh column. The fractions which were supposed to consist mostly of  $\delta$ -hepta were collected, and fractionally recrystallized from isopropyl alcohol, and 0.97g. of crystals were obtained, of which the melting point was  $139\sim 140^\circ$  and the half wave potential was about  $-0.95v$ . The polarogram of this compound is shown in II of Fig.14. This compound did not show the depression of the melting point when mixed with  $\delta$ -hepta which was prepared from  $\gamma$ -BHC by dehydrochlorination and then by chlorination of the dehydrochlorinated compound by *M.Nakazima et al.*<sup>(25)</sup>

#### IV. Separation of Levorotatory Form of $\epsilon$ -hepta

Optically active form of  $\alpha$ -BHC was successfully separated by *S.J.Cristol*<sup>(27)</sup>. The authors applied his method to the separation of L- $\epsilon$ -hepta. Five grams of  $\epsilon$ -hepta, 12.4g. of L-brucine and 50cc of dioxane were allowed to stand at room temperature for 6 days. The alkaloid and alkaloid hydrochloride were removed by washing with water and diluted acid. The mixture was extracted with ether and 3.12g. of oily substance was obtained. This was separated by the partition chromatography and the result is shown collectively in Table 6.

The products of fractions No. 2, and 3 were combined and recrystallized from isopropyl alcohol. Thus, 0.091g. of crystals with a melting point of  $48\sim 49^\circ$  was obtained. This compound did not show the depression of the melting point when mixed with 1,2,3,5-tetrachlorobenzene isolated above.

The products of fractions No. 4, and 5 were combined and recrystallized

†††These were taken by Mr. *K.Kuratani*, Institute of Science and Technology, Tokyo University, and the spectrophotometer used was of Baird make. The wave range measured was  $5.3\mu\sim 16\mu$ . The sample was mixed thoroughly with paraffin oil in solid form.



Table 6: Illustrating the Collection of Percolate Fractions and their Classification from one Product obtained by Reacting  $\epsilon$ -hepta with L-Brucine (3.12 g. of petroleum ether soluble material placed on the column).

Fraction		Description	Classification
No. *	Weight g.		
1	trace	oil; slightly colored	unknown
2	0.21	"	tetrachlorobenzene
3	0.26	solution; slightly colored	tetrachlorobenzene, and hexachlorocyclohexene
4	0.30	oil; colorless	hexachlorocyclohexene, and a little $\epsilon$ -hepta
5	0.31	crystals, containing some oil; colorless	hexachlorocyclohexene, and $\epsilon$ -hepta
6	0.37	oily solid; colorless	$\epsilon$ -hepta, and a little hexachlorocyclohexene
7	0.33	"	$\epsilon$ -hepta
8	0.29	"	"
9	0.37	"	"
10	0.21	"	"
11-16	trace	oil; slightly colored	unknown

\* 20cc fractions, No. 1 being 120-140cc fraction.

from isopropyl alcohol. Then 0.082g. of crystals were obtained with a melting point of  $100\sim 101^\circ$  and this compound did not show the depression of melting point when mixed with an isomer of 1,2,3,4,5,6-hexachlorocyclohexene of mp.  $100\sim 101^\circ$  described above.

The products of the fractions No.6, 7, and 8 were combined and recrystallized from isopropyl alcohol. Then 0.41g. of crystals with a melting point of  $53\sim 54^\circ$  were obtained, and its polarogram was the same as that of original  $\epsilon$ -hepta. The specific rotation and the chlorine analysis were as follows:

$$[\alpha]_{\text{Hg:5461\AA}}^{23^\circ} = -21.6^\circ$$

		Sample(mg.)	AgCl(mg.)	Cl(%)
Found	No. 1	21.9	67.5	76.29
	No. 2	20.2	60.3	76.68
Calcd.	$\text{C}_6\text{H}_5\text{Cl}_7$			76.32

These results indicate that this compound is L- $\epsilon$ -hepta.

### SUMMARY

(1). A new isomer of 1,1,2,3,4,5,6-heptachlorocyclohexane ( $\epsilon$ -form) with a melting point of  $55\sim 55.5^\circ$  was obtained by chlorinating  $\gamma$ -, and  $\alpha$ -BHC, and monochlorobenzene.

(2). A levorotatory form of  $\epsilon$ -hepta was separated by reacting  $\epsilon$ -hepta with L-brucine.

(3). The molecular configurations of  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -BHC;  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -1,1,2,3,4,5,6-heptachlorocyclohexane; o-1,1,2,2,3,4,5,6-octachlorocyclohexane and  $\beta$ -p-1,1,2,3,4,4,5,6-octachlorocyclohexane were determined organic chemically and their chlorine configurations, which are shown by simple notations of p(pole) and e(equatorial), on the chair-form cyclohexane ring are as below:

$\alpha$ -BHC.....	p	p	e	e	e	e
$\gamma$ -BHC.....	p	p	p	e	e	e
$\delta$ -BHC.....	p	e	e	e	e	e
$\epsilon$ -BHC.....	p	e	e	p	e	e
$\alpha$ -hepta .....	$\widehat{pe}$	e	e	e	e	e
$\gamma$ -hepta .....	$\widehat{pe}$	p	e	e	e	e
$\delta$ -hepta .....	$\widehat{pe}$	e	e	p	e	e
$\epsilon$ -hepta .....	$\widehat{pe}$	p	p	e	e	e
o-octo .....	$\widehat{pe}$	$\widehat{pe}$	e	e	e	e
$\beta$ -p-octa.....	$\widehat{pe}$	e	e	$\widehat{pe}$	e	e

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